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ORGANIC CARBON—A NONSPECIFIC WATER QUALITY INDICATOR FOR LAKE SUPERIOR

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Abstract—Organic matter is ubiquitous in surface waters and its presence is generally recognized as being detrimental to water quality. Historically, biochemical oxygen demand (BOD) has been used to assess the effects, and indirectly the concentration, of organic matter in water. However, BOD measurements are not adequate for characterization of high quality natural waters. Measurement of organic carbon by combustion and infrared absorption is a promising technique for monitoring high quality water. This paper is the first part of a study of the distribution of organic carbon in Lake Superior Basin waters. Temporal and spatial distribution of organic carbon in open waters and in the vicinity of pollution inflows are described. Base line concentration levels have been established, and the use of organic carbon measurements as an overall indicator of water quality is discussed.

INTRODUCTION

It is generally recognized that the presence of organic matter in natural waters is detrimental to water quality. The obvious deleterious effects relate to the depletion of dissolved oxygen resulting from biochemical oxidation and the potential public health hazards that stem from public water uses (Rosen, 1970). Concentrates of aquatic organics from the Missouri River have been shown to be toxic (Smith & Giropolous, 1968), and the presence of carcinogens have been reported (Bellar *et al.*, 1974). Historically, biochemical oxygen demand (BOD) has been used to measure pollution levels. However, the BOD test is not adequate for characterization of relatively unpolluted waters because it is not sufficiently sensitive, and it measures only the biodegradable fraction of the organics. More recently, the use of an instrumented method (Van Hall & Stenger, 1967) for total organic carbon (TOC) by combustion and infrared absorbtion has received attention. TOC is a non-specific test that determines the presence of reduced carbon, but does not differentiate between biodegradable and biochemically or chemically refractory materials. The use of TOC in place of BOD in wastewater treatment has been suggested (Emery *et al.*, 1971) but BOD and TOC are not equivalent as evidenced by the difference in BOD/TOC ratios for organic matter of different composition (Davis, 1971). TOC is more sensitive than BOD at the low concentrations normally found in surface waters, and also requires much less time, 2 min versus 5 days for BOD (Maier *et al.*, 1974). The application of TOC measurements for ambient water quality monitoring has been described (Maier *et al.*, 1975) and a number of state monitoring programs now measure TOC routinely. It is, however, noteworthy that there has been no concerted effort to establish the concentration levels of TOC in large lakes, and more specfically to assess the value of TOC measurements as an indicator of overall water quality in relatively unpolluted lakes.

The protection of water quality in the Great Lakes is a major interest of both U.S. and Canadian governments. Lake Superior is of particular concern because of its uniquely high water quality. Measurements of BOD are not sufficiently sensitive to characterize these high purity waters, and cannot reliably detect small changes that could herald large long term effects. With this in mind, a study of carbon concentrations in Lake Superior was carried out and is reported in this paper. Temporal and spatial distributions are discussed, as are base line concentration levels and the use of organic carbon measurements as an overall indicator of water quality. A subsequent paper will deal with the total organic carbon budget of Lake Superior, and will consider the effects of the major inflows and outflows.

SOURCES OF ORGANICS

Aquatic organics consist of varying proportions of materials from natural and anthropogenic sources. Decay of leaf materials, forest litter, and soil organics (humus) are known to be a major source of organics in surface waters (Cummins *et al.*, 1972). Organic carbon concentrations of 5–17 mg l^{-1} have been measured in several lakes in Uppland, Sweden, and correlations between organic carbon, water color, and chlorophyll noted (Forsberg, 1967). Plankton are a substantial source of organics in some lakes. The kinetics of extracellular release of trace organic matter by plankton have been discussed (Saunders, 1972). Contributions from aquatic macrophytes have been described (Wetzel *et al.*, 1972), but the composition and ultimate fate of organic substances are not known. The input of organic materials from municipal and industrial wastes is generally reported in terms of BOD. Anthropogenic inputs include readily biodegradable human and animal wastes and highly refractory and in some cases toxic industrial chemicals such as solvents, pesticides and lignin

derivatives from industrial sources. Treated municipal wastewaters typically contain 15–30 mg l^{-1} BOD which corresponds to 30–80 mg l^{-1} TOC.

The relative contribution of organic substances from natural and anthropgenic sources obviously depends on the extent of industrialization, land use patterns and the level of pollution abatement efforts of the region. The fact that BOD does not measure all the organic materials clearly suggests the need for other measurements.

ANALYTICAL AND SAMPLING PROCEDURES

The instrumental method for combustion and infrared absorption to measure carbon is outlined in Standard Methods for the Examination of Water and Wastewater (1973). An early model Beckman Carbonaceous Analyzer was modified by redesigning the condenser system to improve sensitivity and precision. Total carbon and inorganic carbon were measured on each sample and organic carbon was obtained by difference. Organic carbon measured after 0.45 μm filtration to remove particulates is referred to in the literature as dissolved organic carbon (DOC). The need for measuring particulates depends on the water source; oligotrophic Lake Superior water has negligible concentrations of particulates so that the samples were not filtered. Samples were stored in glass bottles used exclusively for the low carbon content waters and refrigerated until analyzed. Reproducibility of the instrument is good. Repeat analysis of Lake Superior water inorganic carbon concentration (TIC) by the same analyst, on the same day gave a standard deviation of 0.1 mg l^{-1}; TIC measurements on 18 samples from different locations in the open waters of Lake Superior tested at different times show a standard deviations of 0.5 mg l^{-1}. This includes variations associated with sampling as well as spatial differences in TIC concentrations in the lake waters. The practical lower limit for carbon measurement for routine monitoring is approximately 1 mg l^{-1}. In this study samples were tested in triplicate or until reproducible results were obtained and average values are reported to the nearest 0.1 mg l^{-1}.

Near shore and open waters

Samples were obtained through the Lake Superior Basin Studies Center at the locations shown in Fig. 1; water was taken from shipboard at the surface (top 6 in.) and at depths of five feet. Some sampling locations were chosen with a view to measuring open waters removed from land mass effects in areas adjacent to relatively undeveloped land (Stations 1–9); stations 10–14 are representative of waters where quality was likely to be influenced by inflows of pollutants. Organic and inorganic carbon concentrations are listed in Tables 1a and 1b. Organic carbon concentrations (TOC) are consistently low in open waters removed from large surface inflows and sources of pollution (Stations 1–9). TOC ranges from <1.0 to 2.5 mg l^{-1} with an average value of 1.1 mg l^{-1}. Inorganic carbon (TIC) averages 8.8 mg l^{-1}, ranging from 8 to 10 mg l^{-1}. Concentrations at the surface and five foot depths are indistinguishable which is consistent with the fact that the epilimnetic layer is well mixed. Organic carbon concentrations in waters adjacent to large inflows of surface waters and sources of pollution are listed in Table 1b; organic carbon concentration at stations 10–14 range from 3 to 101 mg l^{-1}, and are, in all cases, significantly higher (5% significance level) than stations 1–9. Jackfish Bay waters are grossly polluted; the waters at Ontonagan Harbor and Five Mile Point show the influence of organic inputs, probably from paper mills. Inorganic carbon concentrations are also significantly higher, 10.5–29 compared to the average of 8.8 mg l^{-1} for stations 1–9. The increase in TIC may be the result of biological decay of some of the organic matter and attendant CO_2 production. The lower inorganic carbon concentrations in the Huron Bay samples are ascribed to the higher water temperatures in the bay waters and the growth of algae: algal blooms were reported in near shore waters by the sampling crew.

Comparison of carbon concentrations at stations 10–14 versus 1–9 clearly demonstrates that pollutant inflows have a regional effect and that TOC measurements can be used to detect area-wide as opposed to lake-wide changes in water quality.

Land mass effects

Waters in the proximity of the shoreline, but removed from direct large scale inflows were obtained at several locations along Minnesota's northshore to determine whether there is a land mass effect on water quality. As shown in Table 2, TOC and TIC concentrations in the vicinity of Duluth, but away

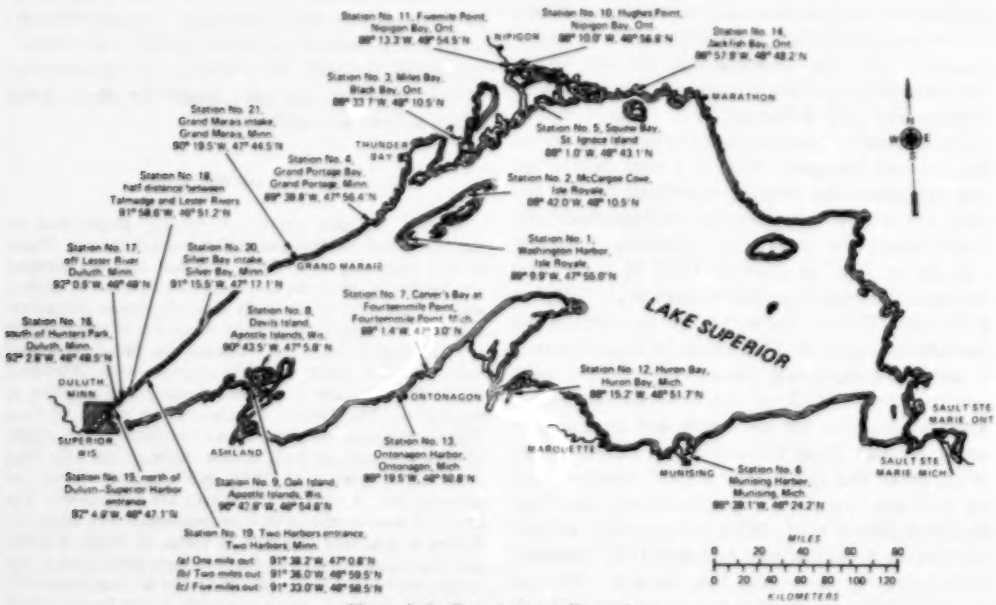
Station No. 11, Fivemile Point, Nipigon Bay, Ont. 88° 13.3' W, 49° 54.5' N
Station No. 10, Hughes Point, Nipigon Bay, Ont. 88° 10.0' W, 49° 56.8' N
NIPIGON
Station No. 14, Jackfish Bay, Ont. 86° 57.9' W, 48° 48.2' N
Station No. 3, Miles Bay, Black Bay, Ont. 88° 33.7' W, 48° 10.5' N
MARATHON
Station No. 21, Grand Marais intake, Grand Marais, Minn. 90° 19.5' W, 47° 44.5' N
Station No. 5, Squaw Bay, St. Ignace Island 88° 1.0' W, 48° 43.1' N
THUNDER BAY
Station No. 4, Grand Portage Bay, Grand Portage, Minn. 89° 39.8' W, 47° 56.4' N
Station No. 18, half distance between Talmadge and Lester Rivers 91° 58.6' W, 46° 51.2' N
Station No. 2, McCargoe Cove, Isle Royale 88° 42.0' W, 48° 10.5' N
Station No. 1, Washington Harbor, Isle Royale 88° 9.9' W, 47° 55.0' N
Station No. 17, off Lester River Duluth, Minn. 92° 0.5' W, 46° 49' N
Station No. 20, Silver Bay intake, Silver Bay, Minn. 91° 15.5' W, 47° 17.1' N
GRAND MARAIS
Station No. 7, Carver's Bay at Fourteenmile Point, Fourteenmile Point, Mich. 88° 1.4' W, 47° 3.0' N
Station No. 16, south of Hunters Park, Duluth, Minn. 92° 2.8' W, 46° 48.5' N
Station No. 8, Devils Island, Apostle Islands, Wis. 90° 43.5' W, 47° 5.8' N
LAKE SUPERIOR
DULUTH MINN.
Station No. 12, Huron Bay, Huron Bay, Mich. 86° 15.2' W, 46° 51.7' N
ONTONAGON
SUPERIOR WIS.
ASHLAND
Station No. 13, Ontonagon Harbor, Ontonagon, Mich. 89° 19.5' W, 46° 50.8' N
MARQUETTE
SAULT STE MARIE ONT.
MUNISING
Station No. 6, Munising Harbor, Munising, Mich. 86° 39.1' W, 46° 24.2' N
SAULT STE MARIE MICH.
Station No. 15, north of Duluth–Superior Harbor entrance 92° 4.6' W, 46° 47.1' N
Station No. 9, Oak Island, Apostle Islands, Wis. 90° 42.6' W, 46° 54.6' N
Station No. 19, Two Harbors entrance, Two Harbors, Minn.
(a) One mile out: 91° 38.2' W, 47° 0.8' N
(b) Two miles out: 91° 36.0' W, 46° 59.5' N
(c) Five miles out: 91° 33.0' W, 46° 58.5' N
MILES
0 20 40 60 80
0 20 40 60 80 100 120
KILOMETERS

Fig. 1. Lake Superior sampling points.

Table 1a. Lake Superior carbon concentrations

Station number*	Location	Depth	Date	Carbon concentration, mg l^{-1} organic	inorganic	Comparison with IJC water quality objective
1	Wash. Hrbr. Isle Roy.	Surface	6–7–75	0.1	9.1	o.k.
	Wash. Hrbr. Isle Roy.	5 ft	6–7–75	2.5	8.5	o.k.
2	McCargoes Cove	Surface	6–8–75	1.9	8.4	o.k.
	McCargoes Cove	5 ft	6–8–75	1.2	9.0	o.k.
3	Miles Bay, Black Bay	Surface	6–10–75	1.5	9.4	o.k.
	Miles Bay, Black Bay	5 ft	6–10–75	1.7	9.1	o.k.
4	Grand Portage Bay	Surface	6–11–75	0.3	8.2	o.k.
	Grand Portage Bay	5 ft	6–11–75	1.2	8.2	o.k.
5	Squaw Bay, Ont.	Surface	6–14–75	0.3	8.7	o.k.
	Squaw Bay, Ont.	5 ft	6–14–75	1.0	8.8	o.k.
6	Munising Harbor	Surface	6–20–75	2.2	9.9	o.k.
	Munising Harbor	5ft	6–20–75	0.2	9.3	o.k.
7	14 Mile Pt. Mich.	Surface	6–23–75	1.7	9.2	poorer
	14 Mile Pt. Mich.	5 ft	6–23–75	1.8	8.6	poorer
8	Apostles Is. Devil's Is.	Surface	6–26–75	1.2	8.3	o.k.
	Apostles Is. Devil's Is.	5 ft	6–26–75	0.7	8.3	o.k.
9	Oak Island	Surface	6–26–75	0.4	8.5	o.k.
	Oak Island	5 ft	6–26–75	0.7	8.5	o.k.
Average of Stations 1–9				1.1	8.8	

* Locations are illustrated in Fig. 1.

Table 1b. Lake Superior carbon concentrations

Station number*	Location	Depth	Date	Carbon concentration mg l^{-1} organic	inorganic	Comparison with IJC water quality objective
10	Hughes Point, Nipigon Bay	Surface	6–12–75	3.4	13.3	poorer
	Hughes Point, Nipigon Bay	5 ft	6–12–75	2.8	13.3	poorer
11	5 Mi. Pt. Nipigon Bay	Surface	6–12–75	5.3	12.9	poorer
	5 Mi. Pt. Nipigon Bay	5 ft	6–12–75	5.8	13.3	poorer
12	Huron Bay, Mich.	Surface	6–21–75	5.2	7.4	poorer
	Huron Bay, Mich.	5 ft	6–21–75	5.2	7.0	poorer
13	Ontonagon Mich. Hr. 2000	Surface	6–23–75	18.1	10.5	poorer
	Ontonagon Mich. Hr. 2000	5 ft	6–23–75	17.7	10.5	poorer
14	Jackfish Bay, Ont.	Surface	6–16–75	101.0	28.7	poorer
	Jackfish Bay, Ont.	5 ft	6–16–75	56.8	21.7	poorer

* Locations are shown in Fig. 1.

Table 2. Carbon concentrations in near shore waters

Station number*	Location	Date	Average carbon concentrations, mg l^{-1} organic	inorganic
	Vicinity of Duluth			
15	North of Harbor entrance (6)	3–14–75	2.5	9.6
16	South of Hunter Park (4)	3–14–75	1.8	9.4
17	Near Lester River (4)	3–14–75	2.1	9.2
18	Half distance between Talmadge	3–14–75		
	and Lester River (4)		2.1	9.5
	Average		2.1	9.4
19	Two Harbors Entrance			
	a. 1 mile out (5)		1.7	8.5
	b. 3 miles out (3)		1.5	8.5
	c. 5 miles out (4)		1.7	8.7
	Average		1.6	8.6
20	Silver Bay			
	Water Plant intake (17)	monthly	1.0–6.0	4.8–9.5
	Average		2.1	7.6
21	Grand Marais			
	Water Plant intake (11)	monthly	0–5.2	5–10.2
	Average	samples	2.0	7.7

( ) number of samples tested.
* Locations are shown in Fig. 1.

from the harbour area, range from 1.8 to 2.5 and 9.2 to 9.6 respectively. Near shore TOC concentrations are approximately 1 mg l^{-1} higher than open water samples; TOC averages 2.1 versus 1.1 mg l^{-1} and TIC averages 9.4 versus 8.8. The samples outside of the Two Harbors area are probably more representative of open water having been taken some 1–5 miles off shore. Water samples at the Silver Bay and Grand Marais water plant intake average 2 mg l^{-1} organic carbon. This suggests that the shoreline effect is similar to that noted in the Duluth vicinity. Reported mean TIC concentrations are lower because they are year-round average values reflecting lower inorganic carbon concentration during winter months.

Duluth–Superior Harbor area

Water quality in the harbor area of Duluth–Superior is of particular concern because it receives considerable inflow of urban wastes. The harbor is protected from lake currents by a finger of land that closes off the harbor area except for two exits at the north and southeast as illustrated in Fig. 2. The St. Louis and Nemadji Rivers flow into the bay. Water samples from the harbor area were tested on two occasions (3/6/75 and 4/10/75) to determine carbon concentrations at different water depths and to evaluate the effects of passage of ships on sediment resuspension and thus on carbon distribution. Three replicate samples were obtained at 5 and 25 foot depths at each of two stations identified as Nos. 22 and 23 in Fig. 2 before and after passage of large ships. As shown in Table 3, both TOC and TIC concentrations of harbor waters are high, 12 and 17 mg l^{-1} respectively; carbon concentrations are remarkably uniform at both sampling stations and at the 5 and 25 ft depths. The most significant difference in carbon concentration is the increase in TIC from 3/6/75 to 4/10/75. This is believed to be a seasonal phenomenon that mirrors seasonal variations observed in the St. Louis River (Maier *et al.*, 1975). Comparison of the data before and after passage of ships shows a small, but statistically significant increase in TOC, averaging 0.6 mg l^{-1}. However, the increase is inconsequential considering the overall water quality in the habor. The passage of large vessels caused a visible scouring of bottom sediment materials with an associated vertical mixing of bottom water that contained higher dispersed organic contents. The harbor shipping channels are nominally dredged to a depth of 30 ft. A fully loaded commercial bulk carrier has a draft of approximately 28 ft 8 in. at the stern. The mechanical

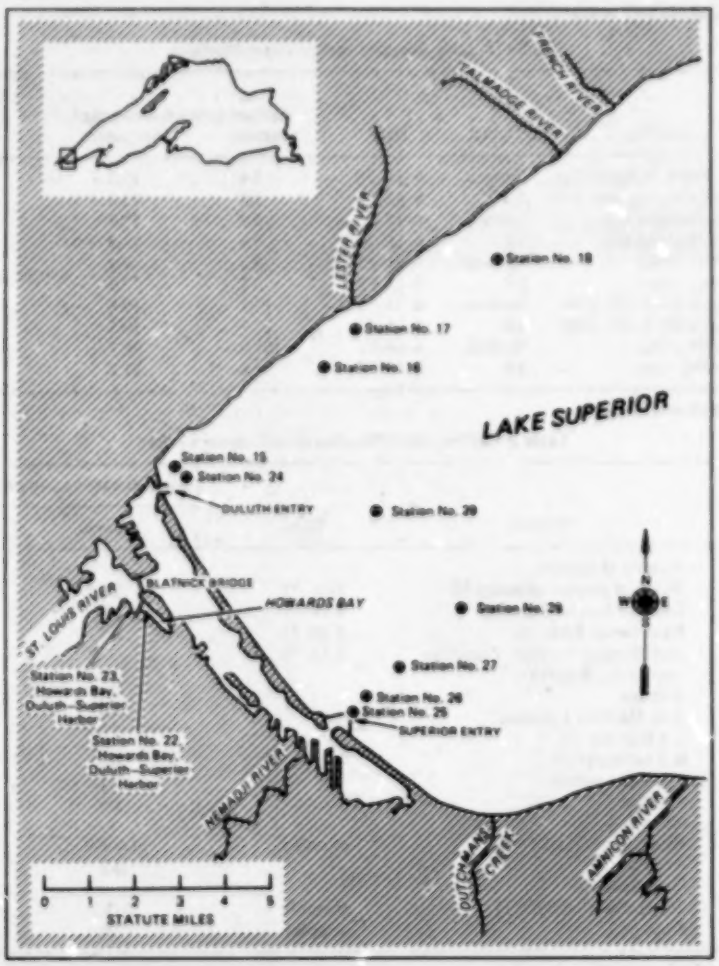

Fig. 2. Duluth–Superior Harbor area sampling points.

Table 3. Carbon concentrations Duluth–Superior Harbor

Date	Station number*	Depth ft	Organic, mg l^{-1} after		before	Inorganic, mg l^{-1} after		before
4–10–75	23	5	12.3		11.5	19.4		19.7
4–10–75	23	25	13.1		12.2	17.7		19.6
4–10–75	22	5	12.8		11.3	19.0		20.3
4–10–75	22	25	12.7		12.8	18.6		18.3
Sub average				12.3			19.1	
3–6–75	23	5	12.3		12.9	14.5		14.1
3–6–75	23	25	12.1		11.9	15.7		15.4
3–6–75	22	5	13.5		13.3	15.8		15.6
3–6–75	22	25	14.3		12.9	14.4		15.6
Sub average				12.9			15.1	
Overall average				12.6			17.1	

Station No. 22—Howard's Bay over Corps of Engineer's bubbler.
Station No. 23—Howard's Bay 125 ft north of Farmer's Union Elevator No. 1.
* Locations are illustrated in Fig. 2.
Before and after refer to passage of large ships.

agitation by the ship's screw quite easily entrains particulates from the bottom sediments. Long dispersive plumes of this material are not an uncommon sight in the wake of large freighters in the shallow waters of the harbor.

Comparison of the harbor waters with unpolluted open water, 12.6 versus 1.1 mg l^{-1} TOC, illustrates the degree of water quality deterioration in the harbor area. High TOC levels are due to the combined influx of organics from the St. Louis and Nemadji Rivers and urban drainage. One important consequence of the inflow of river waters is that the polluted harbor water is continually being displaced into the lake. The finger of land that protects the harbor from lake currents therefore slows down the dispersion process, but does not stop the pollutants from being discharged to the lake. Studies of the flow pattern indicate that some 60% of effluent waters from the St. Louis River find their egress from the Duluth Ship Canal, the northern harbor entrance; the remaining 40% exit from the Superior Harbor entry, the southern harbor opening, along with the runoff from the Nemadji River (Sydor, 1976).

The dispersion of low quality harbor water into open lake waters is illustrated by the carbon concentration gradients in the vicinity of the harbor exits (Table 4). Samples obtained 0.6 miles northeast of the northern harbor entrance average 5.2 mg l^{-1} TOC compared to 1.5 mg l^{-1} in open lake water four miles away. Water samples taken approximately 0.1 miles from the southern harbor entrance average 13 mg l^{-1} TOC which is essentially the same as in the harbor. TOC concentrations decrease with distance (direction east northeast) from the entrance, 4.9 mg l^{-1} at 0.7 miles, 4.2 mg l^{-1} at 1.6 miles, and 3.9 mg l^{-1} at 3.4 miles. This pattern of dispersion is consistent both with the direction of prevailing currents that flow through the western part of the lake and with repeated multispectral scans and remote sensing imagery from high and low level overflights and satellite observations (Sydor & Swain, 1976). Concentrations of organic carbon would be expected to fluctuate considerably in the areas east and northeast of the southern tip depending on current velocities and hence dilution–dispersion.

DISCUSSION

The observation that waters in the proximity of the shore have higher carbon concentrations than open waters is not unexpected. Surface runoff and plankton productivity in the warmer shallow shoreline waters are potential sources of organic inputs. Shoreline or land mass effects have been reviewed (Higuchi, 1975); effects on primary productivity (photosynthesis) have been observed in oceanic waters (Strickland, 1965), in large freshwater lakes (Vollenweider *et al.*, 1974) and in Lake Superior (Fox *et al.*, 1969). Inshore areas usually have higher average cell counts and more

Table 4. Duluth–Superior Harbor and vicinity

Station number*	Location	Average carbon content, mg l^{-1} TOC	TIC
24	0.6 miles NE north entrance	5.2 (6)	10.1 (6)
25	0.1 mile NE south entrance	13.0 (3)	12.4 (3)
26	0.7 miles NE south entrance	4.9 (3)	11.1 (3)
27	1.6 miles NE south entrance	4.2 (3)	8.9 (3)
28	3.4 miles NE south entrance	3.4 (3)	9.0 (3)
29	Open water—4.6 miles equidistant from north and south entrance	1.5 (3)	8.8 (3)

Sampled March 31–April 1, 1976.
( ) number of samples.
* Locations are illustrated in Fig. 2.

numerous peaks in biomass throughout the growth season. Nevertheless, it is unlikely that plankton biomass in Lake Superior could account for the consistently higher organic concentration of near shore waters (2 versus 1 mg l^{-1}). Data on particulate carbon concentration associated with plankton in Lake Superior are not available, but even mesotrophic Lake Ontario has less than 0.5 mg l^{-1} particulate carbon (Vollenweider *et al.*, 1974). Contributions of organic carbon from macrophytes (Wetzel, 1972) and extracellular release of organics by plankton (Saunders, 1972) are contributing sources, but the quantities from these sources are likely to be small. The most plausible explanation for the near shore increase in TOC is the nonpoint source runoff from the land mass which is known to contribute substantial amounts of refractory organics (Maier *et al.*, 1975).

Analysis of the Lake Superior TOC data shows that there is a quantitive relationship between organic carbon concentration and overall water quality. The last column in Table 1 identifies those sampling stations that do not meet the water quality objectives of the International Joint Commission (IJC, 1973). The IJC quality objectives include consideration of phosphorous, nitrogen, biochemical oxygen demand concentrations and turbidity. All samples that fail to meet IJC water quality objectives also have high TOC concentrations with the exception of No. 7 at 14 Mile Point in Michigan. However, this location had been identified by the IJC as an area high in chlorides resulting from mine drainage into the Mineral River (IJC, 1973). The TOC data fell into three categories:

	TOC range, mg l^{-1}
(1) Open waters	>1.5
(2) Areas of water influenced by land mass effects and/or surface inflows	2–5
(3) Grossly polluted areas of water	5+

Measurements of TIC show similar trends, but TIC concentrations are more time-variable. Variations in bacterial decay rates and/or photosynthesis can bring about rapid localized changes in TIC.

The water quality of Lake Superior is so high that early signs of irreversible damage may go undetected because it is difficult to document changes at very low concentration levels using conventional measures of pollution such as BOD and volatile solids. Using the standards of clean water normally considered appropriate for pollution control programs, Lake Superior could be degraded significantly and irreversibly before water quality changes could be documented. The measurement of organic carbon as TOC or DOC shows promise as a monitoring and detection method to give early warnings of water quality deterioration. Consideration should be given to setting organic carbon concentration criteria for water quality planning goals and objectives.

The potential value of organic carbon measurements for assessing long term trends in Lake Superior water quality are discussed in a companion paper entitled Lake Superior Organic Carbon Budget, which has been accepted for publication in this journal.

SUMMARY

Baseline concentrations of organic and inorganic carbon concentration in Lake Superior have been established. Open water remote from sources of pollution average 1.1 mg l^{-1} TOC. TIC ranges from 8 to 10 mg l^{-1}, but varies seasonally. Concentrations of TOC at the five foot level are indistinguishable from surface samples. Area-wide increases in TOC and TIC have been detected in the vicinity of point sources of pollution. TOC values range from 3 to 101 mg l^{-1}, the higher value is indicative of gross pollution. Shoreline or land mass effects were observed in all near-shore samples. TOC values were approximately 1 mg l^{-1} higher than in open waters and TIC concentrations were also somewhat higher. Waters in the Duluth–Superior Harbour area were significantly higher, averaging 12.6 mg l^{-1} and 17.1 mg l^{-1}, TOC and TIC respectively. The effects of polluted harbor waters were detectable for at least 5 miles beyond the harbor limits.

Analysis of the TOC concentration data in conjunction with the water quality criteria used by the International Joint Commission for the Great Lakes shows that high TOC concentrations correlate with poor water quality. A scale relating TOC and water quality for Lake Superior has been formulated. Analytical tools for measuring TOC and TIC are readily available and can be used for routine surveillance and monitoring. TOC measurements are sufficiently sensitive to detect small changes (1 mg l^{-1}). For Lake Superior TOC concentrations greater than 1.5 mg l^{-1} are indicative of pollution. The long range effect of present levels of pollutant inflows is unknown. Open waters and the waters adjacent to large inflows should be monitored to assess the need for more stringent controls.

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REFERENCES

Bellar T. A., Lichtenberg J. J. & Kroner R. C. (1974) The Occurence of Organohalides in Chlorinated Drinking Waters, *J. Am. Water Wks Ass.*, **66**, 12, 703–706.

Cummins K. W., Klug J. J., Wetzel R. G., Peterson R. C., Suberkropp K. F., Manny B. A., Waycheck J. C., & Howard D. O. (1972) Organic Enrichment with Leaf Leachate in Experimental Lotic Ecosystems, *Bio Sci.* **22**, 719–722.

Davis E. M. (1971) "BOD vs COD vs TOD", *Water Wastes Engng.* **8**, 2, p. 32.

Emery R. M., Welch E. B., & Christman R. F. (1971) The Total Organic Carbon Analyzer and its Application to Water Research, *J. Wat. Pollut. Control Fed.*, **43**, 1834.

Forsberg D. (1967) Dissolved Organic Carbon in Some Lakes in Uppland, Sweden, Oikos, **18**, 210.

Fox J. L., Odlaug T. O., & Olson T. A. (1969) The Ecology of Periphyton in Western Lake Superior Part I—Taxonomy and Distribution. *Wat. Resour. Res. Center Bull.* **14**.

Higuchi Isamu, S. (1975) Investigations for Land Mass Effects in Lake Itasca, Minnesota, Private Communication

(IJC) Regulation of Great Lakes Water Levels, Report to the Int. Joint Commission by the Int. Great Lake Levels Board, Dec. 7, 1973.

Maier W. J., McConnell H. L. (1974) Carbon Measurements in Water Quality Monitoring, *J. Wat. Pollut. Control Fed.*, **46**, 623.

Maier W. J., Conroy L. E., Anderson C. (1975) The Occurrence of Organic Carbon in Surface Waters, IAGC–IAHS Intern. Symp. on the Geochemistry of Natural Waters, Canada Center for Inland Waters, Burlington, Canada.

Maier W. J., Gast R. G., Anderson C. T. & Nelson W. W. (1975) Carbon Contents of Surface and Underground Waters in South Central Minnesota, Sci. J. Ser., Minnesota Agricultural Experiment Station.

Maier W. J., Conroy L. E., Anderson C. T. (1975) Survey of Organic Carbon Concentrations in Minnesota Surface Waters, Presented at Annual Meeting Central States Water Pollution Control Federation, Madison, Wisc.

Rosen A. A. Identification of Organic Matter in Polluted Water. Symp. Organic Matter in Natural Waters, Univ. of Alaska, Sept., 1968, Inst. Marine Science. Occasional Publ. No. 1, June 1970, p. 359.

Saunders G. W., Jr. (1972) The Kinetics of Extracellular Release of Soluble Organic Matter by Plankton, *Verh. Internat. Verein. Limnol.* **18**, 162–170,

Smith J. W., Grigoropoulos S. G. (1968) Toxic Effects of Odorous Trace Organics, *J. Am. Wat. Wks Ass.* **60**, 969.

Standard Methods for the Examination of Water and Waste Waters. (1973) 13th Edn., *Am. Publ. Hlth Ass.*

Strickland J. D. H. (1965) Production of Organic matter in the Primary Stages of the Marine Food Chain. In *Chemical Oceanography*. Edited by Riley J. P. & Skirrow. Vol. I, pp. 477–610. Academic Press.

Sydor M. (197[illegible] Personal Communication.

Sydor M. & Swain W. R. (1976) Unpublished data.

Van Hall C.E., Stenger V.A. (1967) An Instrument for the Rapid Determination of Carbonate and Total Carbon in Solutions, *Anal. Chem.* **39**, 503.

Vollenweider R. A., Munawar M. & Stadelman P. (1974) A Comparative Review of Phytoplankton and Primary Production in the Laurentian Great Lakes, *J. Fish. Res. Bd* Can. **31**, 739–762.

Wetzel R. C., Manny B. A. (1972) Secretion of dissolved organic carbon and nitrogen by aquatic macrophytes. *Verh. Internat. Verein. Limnol.* **18**, 162–170.